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1. REPORT DATE (DD-MM-YYYY) 06-06-2016	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 1-Oct-2011 - 30-Sep-2014
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4. TITLE AND SUBTITLE Final Report: Understanding Molecular Ion-Neutral Atom Collisions for the Production of Utracold Molecular Ions	5a. CONTRACT NUMBER W911NF-11-1-0524
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102

6. AUTHORS Eric R. Hudson	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of California - Los Angeles Office of Contract and Grant Administration 11000 Kinross Avenue, Suite 211 Los Angeles, CA 90095 -1406	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 60365-PH.12

12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT In the last five years, the study of ultracold molecular ions has emerged as a new discipline within AMO to bring molecules under control. It is now clear that a trapped sample of ultracold molecular ions affords many of the benefits of ultracold neutral molecules, while significantly reducing experimental complexity – e.g. large trap depths, long trap lifetimes, and efficient detection. Despite the infancy of the field, there is already a clear path to a wide range of important studies, including the investigation of quantum chemistry, precision measurement of molecular transitions, and the implementation of scalable quantum computation architecture.

15. SUBJECT TERMS molecular ion, quantum chemistry, atom ion interaction, photodissociation spectroscopy

16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	UU		Eric Hudson
b. ABSTRACT UU			19b. TELEPHONE NUMBER 310-825-5224
c. THIS PAGE UU			

Report Title

Final Report: Understanding Molecular Ion-Neutral Atom Collisions for the Production of Ultracold Molecular Ions

ABSTRACT

In the last five years, the study of ultracold molecular ions has emerged as a new discipline within AMO to bring molecules under control. It is now clear that a trapped sample of ultracold molecular ions affords many of the benefits of ultracold neutral molecules, while significantly reducing experimental complexity – e.g. large trap depths, long trap lifetimes, and efficient detection. Despite the infancy of the field, there is already a clear path to a wide range of important studies, including the investigation of quantum chemistry, precision measurement of molecular transitions, and the implementation of scalable quantum computation architecture.

Under this award, we performed a series of experiments aimed at understanding the collisional physics between ultracold neutral atoms and molecular ions. This work resulted in several important observations of cold atom-ion photochemistry that were among the first of their kind, and have helped to open the field of cold atom-ion chemistry. In addition to these reactivity studies, we also developed tools for analyzing trapped molecular ions and recording their spectra, as well as solved several longstanding problems regarding trapped ion “thermodynamics”. Finally, using the results of all of this work, we demonstrated that both the vibrational and external degrees of freedom of trapped molecular ions are efficiently cooled by sympathetic cooling collisions with laser-cooled atoms. Thus, through our previous ARO support, we have developed many of the necessary tools and techniques to help open the field of ultracold molecular ion research.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/21/2012	1.00 Wade Rellergert, Scott Sullivan, Svetlana Kotochigova, Alexander Petrov, Kuang Chen, Steven Schowalter, Eric Hudson. Measurement of a Large Chemical Reaction Rate between Ultracold Closed-Shell ^{40}Ca Atoms and Open-Shell $^{174}\text{Yb}^{\{+\}}$ Ions Held in a Hybrid Atom-Ion Trap, Physical Review Letters, (12 2011): 0. doi: 10.1103/PhysRevLett.107.243201
08/21/2012	4.00 Kuang Chen, Steven Schowalter, Svetlana Kotochigova, Alexander Petrov, Wade Rellergert, Scott Sullivan, Eric Hudson. Molecular-ion trap-depletion spectroscopy of $\text{BaCl}^{\{+\}}$, Physical Review A, (3 2011): 0. doi: 10.1103/PhysRevA.83.030501
08/21/2012	3.00 Scott T. Sullivan, Wade G. Rellergert, Svetlana Kotochigova, Kuang Chen, Steven J. Schowalter, Eric R. Hudson. Trapping molecular ions formed via photo-associative ionization of ultracold atoms, Physical Chemistry Chemical Physics, (2011): 0. doi: 10.1039/c1cp21205b
08/21/2012	2.00 Steven J. Schowalter, Kuang Chen, Wade G. Rellergert, Scott T. Sullivan, Eric R. Hudson. An integrated ion trap and time-of-flight mass spectrometer for chemical and photo- reaction dynamics studies, Review of Scientific Instruments, (2012): 0. doi: 10.1063/1.3700216
10/01/2013	5.00 Scott T. Sullivan, Wade G. Rellergert, Svetlana Kotochigova, Eric R. Hudson. Role of Electronic Excitations in Ground-State-Forbidden Inelastic Collisions Between Ultracold Atoms and Ions, Physical Review Letters, (11 2012): 0. doi: 10.1103/PhysRevLett.109.223002
10/01/2013	6.00 Kuang Chen, Scott T. Sullivan, Wade G. Rellergert, Eric R. Hudson. Measurement of the Coulomb Logarithm in a Radio-Frequency Paul Trap, Physical Review Letters, (04 2013): 0. doi: 10.1103/PhysRevLett.110.173003
10/01/2013	7.00 Wade G. Rellergert, Scott T. Sullivan, Steven J. Schowalter, Svetlana Kotochigova, Kuang Chen, Eric R. Hudson. Evidence for sympathetic vibrational cooling of translationally cold molecules, Nature, (03 2013): 0. doi: 10.1038/nature11937
TOTAL:	7

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Steven J. Schowalter	0.50	
Scott Sullivan	0.50	
FTE Equivalent:	1.00	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Alexander Dunning	0.70
Christian Schneider	0.20
FTE Equivalent:	0.90
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Eric R Hudson	0.08	
FTE Equivalent:	0.08	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Prateek Puri	0.20	
FTE Equivalent:	0.20	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 3.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 3.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 3.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 1.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attached.

Technology Transfer

The primary focus of our effort was to produce ultracold molecular ions via sympathetic cooling with laser cooled atoms. Building on the atom-ion chemistry and molecular spectroscopy work of previous years, we performed several proof-of-principle experiments that have demonstrated, for the first time, sympathetic cooling of both the translational and vibrational motion of BaCl^+ molecules through collisions with ultracold gases. These experimental results have indicated that the proposed cooling method is as efficient as expected. We have also spent significant time understanding the details of the cooling mechanisms so that the experimental system can be optimized. Work has now turned to the next generation of experiments.

In what follows we give brief description of each effort undertaken during the project.

Introduction to the experimental system (MOTION trap): The construction of the original MOTION trap system was completed in late 2010 and is shown in the accompanying photo and figure below. At the center of the vacuum chamber is the ^{40}Ca magneto-optical trap (MOT) co-located with a linear quadrupole radio-frequency ion trap (LQT) system. The ^{40}Ca MOT laser beams (blue) are evidenced by scattered light from the optics. The necessary computer and laser controls can be seen in the background. Using this system we have studied the MOTION trap environment as detailed below.

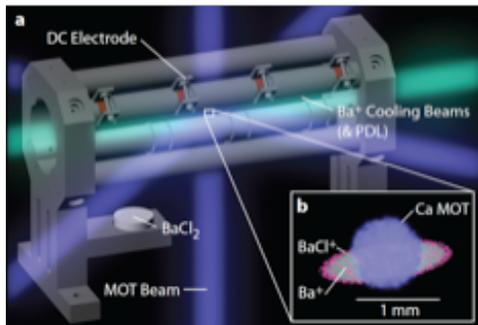
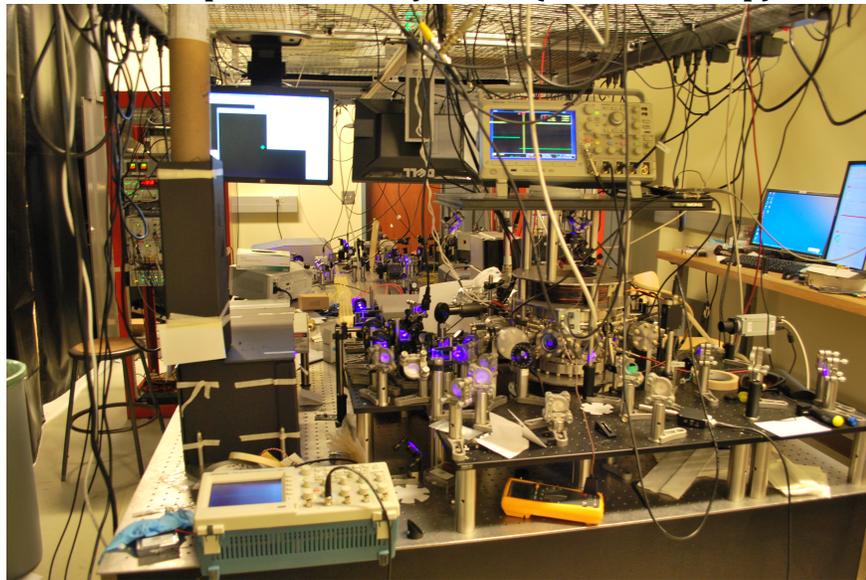


Figure 1. First-generation MOTION trap system. Molecular and/or atomic ions that have been produced by laser ablation of a solid target are trapped in the middle chamber of the linear quadrupole trap, while ultracold atoms are collected in a MOT. The ultracold atoms quickly cool the atomic/molecular ion's external and internal degrees of freedom.

Work towards understanding the kinematics of sympathetic cooling in an ion trap: Since the work of Dehmelt over forty years ago, it has been known that sympathetic cooling in an ion trap environment is much more complicated than in a static trap. However, an accurate, complete description of the effects observed in these systems has never been presented. We have explored both theoretically and experimentally. We have now developed a complete understanding of the processes at play. These effects stem from the occurrence of collisions in the presence of the radio-frequency (rf) trapping voltages of the ion trap and allow for energy to be coupled from the rf trap field into the motion of the ion. This work has resulted in one manuscript to-date and another is in preparation: K. Chen et al., Phys. Rev. Lett. **110**, 173003 (2013) (Editor's suggestion) and K. Chen et al., Phys. Rev. Lett. **112**, 143009 (2014). Finally, we believe this work will continue to be fruitful for the foreseeable future, as we have recently discovered that these effects lead to a rich system exhibiting power law energy distributions and non-equilibrium steady state physics.

Demonstration of the production of cold molecular ions: Using the MOTION trap system we implemented a two-stage sympathetic cooling procedure to cool BaCl⁺. Trapped BaCl⁺ ions were immersed in laser-cooled clouds of Ba⁺ ions and Ca atoms. Due to the strong Coulomb interaction, the Ba⁺ ions quickly cool the molecular ion translation motion, while the neutral Ca atoms cool the BaCl⁺ molecular ion internal degrees of freedom (rovibrational quantum states) via short-range atom-ion sympathetic cooling collisions. As shown in Fig. 2, which plots the results of a photodissociative thermometry measurement, the molecular ions have been cooled to the vibrational ground state with ~90% probability. This work demonstrates the principles of the ultimate goal of this proposal. We expect this work to be of high impact in the field as it represents a simple, generic method for producing cold molecular ions, and thus enables a host of technologies and fundamental physics, as outlined in our proposal. This work was reported in a manuscript in Nature. [W.G. Rellergert et al., "Sympathetic vibrational cooling of translationally cold molecules," Nature **495**, 490 (2012)].

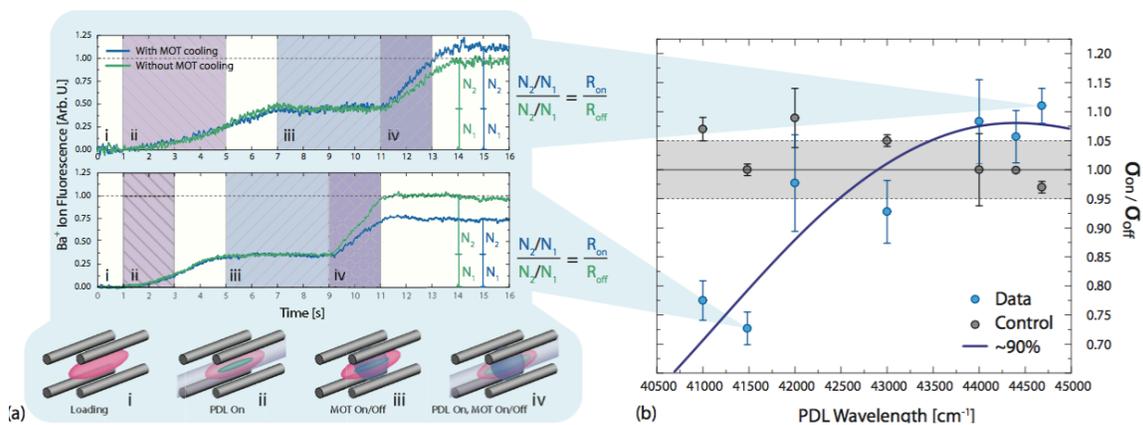


Fig. 2. (Left) Fluorescence of Ba⁺ ions produced via photodissociation of BaCl⁺ as a function of time with and without the MOT. The difference in final fluorescence values is a direct result of the BaCl⁺ internal state temperature and can be used to calculate the molecular vibrational populations. (Right) Results of photodissociation thermometry showing ~90% ground state occupation.

Construction of the next generation MOTION trap: Using what was learned in the sympathetic cooling experiments, we have redesigned and constructed the second generation of the MOTION trap. This system affords single ion imaging and colder final temperatures for the molecular ions. We have also added a unique time-of-flight mass spectrometer to the system, which provides a paradigm shift in how we study of ultracold atom-ion chemistry. This work was a significant undertaking and has required the development of novel rf electronics, all of which have been documented in a technical papers.

This system became fully operational in November of 2013. Already, it has produced exciting results, demonstrating both single ion imaging resolution and new route to improving mass spectrometry. We expect this system to enable a new level of control in both the production of ultracold molecular ions and cold atom-ion chemistry.

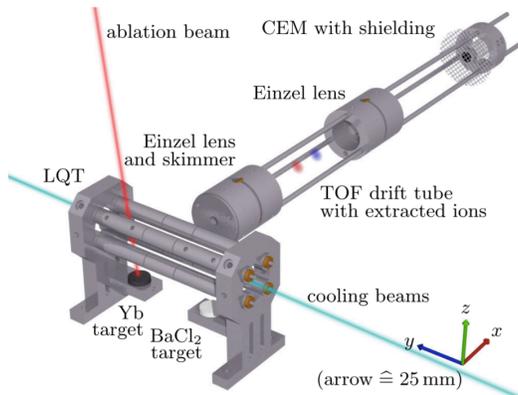


Fig. 3. Schematic of 2nd generation system. The unique radially coupled time-of-flight apparatus provides a new tool for the study of ultracold molecular ions.

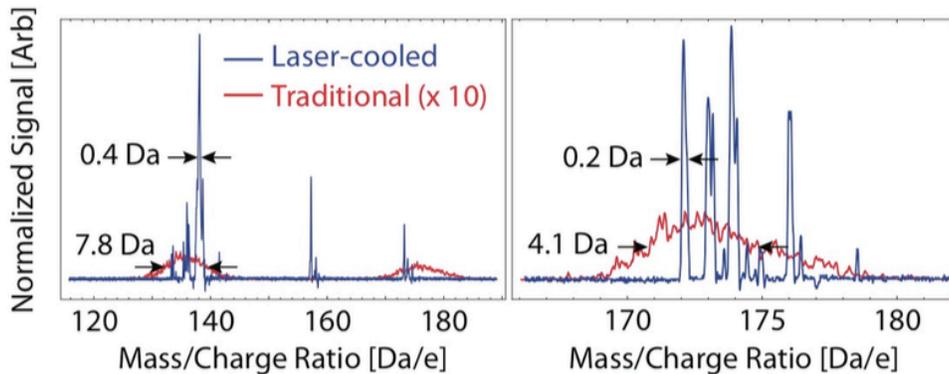


Figure 4. Traditional vs. optimized laser-cooled mass spectra. Left: mass spectrum of the products of laser ablating solid BaCl₂ while laser-cooling ¹³⁸Ba⁺. Right: mass spectrum of the products of laser ablating Yb metal while laser-cooling ¹⁷²Yb⁺. Both the mass resolution and detection efficiency are improved by over an order of magnitude.